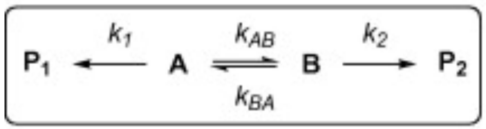
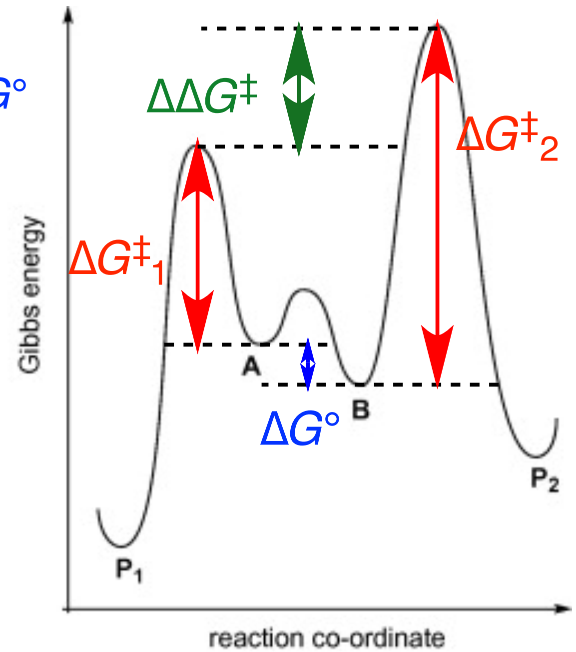
Quick derivation of the Curtin-Hammett Principle

$\Delta\Delta G^{\ddagger} = \Delta G^{\ddagger}_{2} - \Delta G^{\ddagger}_{1} + \Delta G^{\circ}$





First, $d[\mathbf{P_1}]/dt = k_1[\mathbf{A}]$ and $d[\mathrm{P_2}]/dt = k_2[\mathbf{B}]$.

Due to rapid equilibration, we can make the approximation that

$[\mathbf{B}]/[\mathbf{A}] = k_{\mathrm{AB}}/k_{\mathrm{BA}} = K$, so that $d[\mathbf{P_2}]/dt = k_2[\mathbf{B}] = Kk_2[\mathbf{A}]$.

That means that $d[\mathbf{P_2}] = (Kk_2/k_1)d[\mathbf{P_1}]$. Integrating, $[\mathbf{P_2}] = (Kk_2/k_1)[\mathbf{P_1}]$ or

$[\mathbf{P_2}]/[\mathbf{P_1}] = Kk_2/k_1$.

Converting into energies,

$[\mathbf{P_2}]/[\mathbf{P_1}] = \exp(-\Delta G^{\circ}/RT)\exp(-\Delta G^{\ddagger}_{2}/RT)\exp(\Delta G^{\ddagger}_{1}/RT) =$

$\exp[-(\Delta G^{\ddagger}_{2} - \Delta G^{\ddagger}_{1} + \Delta G^{\circ})/RT]$, so

$[\mathbf{P_2}]/[\mathbf{P_1}] = \exp(-\Delta\Delta G^{\ddagger}/RT)$.